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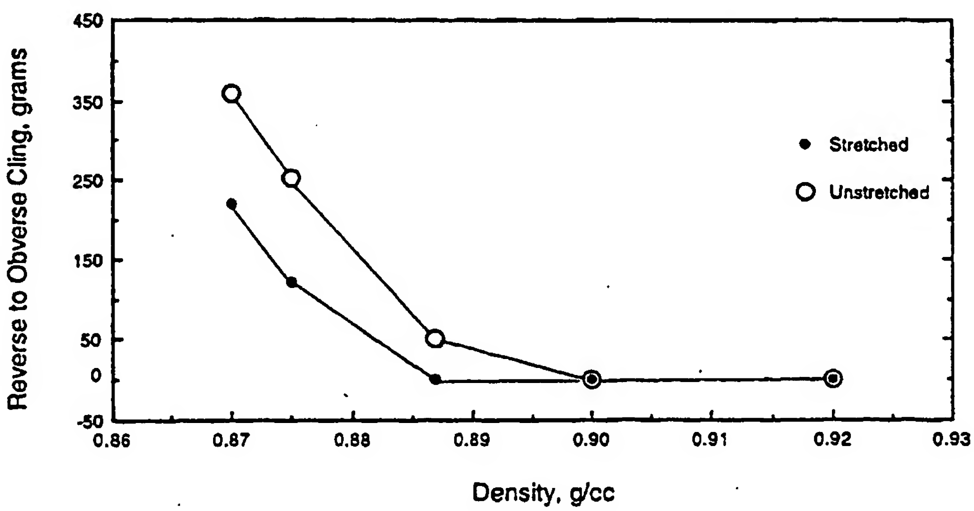


(57) Abstract

Multilayer thermoplastic stretch wrap film having substantial one-sided cling properties is made without the use of polymers with high levels of n-hexane extractables, dissimilar polymer chemistries, or low molecular weight tackifiers. The reverse or cling layer comprises at least one homogeneously branched ethylene polymer composition having a density of about 0.90 g/cc or less and the obverse or non-cling layer comprises a propylene or ethylene polymer composition having a density greater than 0.90 g/cc. The multilayer film is particularly useful for load palletization end-use applications.

STRETCH CLING FILM AND FABRICATION METHOD

This invention pertains to multilayer thermoplastic stretch wrap film, a method for forming such film and the use of such film for load palletization wrapping. The invention particularly pertains to polyolefin stretch wrap film having substantial one-sided cling properties without the use of functional polymers such as ethylene methacrylate copolymers or low molecular weight tackifiers such as polyisobutylene.

Stretch films that self-seal when portions are overlapped are known as "cling" films. These films are most often multilayer films and are used in applications where it's desirable to securely hold and/or wrap an article or group of articles, such as load palletization. For load palletization operations, the film is stretched tightly around the good or plurality of goods situated on a pallet, and self-sealed while the film is still in the stretched condition to create a secure, unitized package. Both unstretched or pre-stretched films are used for load palletization and retention of substantial cling properties and good tear properties while the film is stretch-wrapped are required to maintain the integrity of the unitized load.

There are several deficiencies associated with known cling films. For instance, many cling films are characterized as having substantial cling properties on both their outer ("obverse") layer and their inner ("reverse") layer. These two-sided cling films retain unsightly dirt and dust and undesirably adhere to adjacent goods and similarly wrapped packages when abutted against one another. Adhesion to adjacent goods and packages typically causes ripping, tearing, distortion and/or unraveling of the film during subsequent handling.

As disclosed in U.S Pat. Nos. 5,175,049 and 3,025,167, cling films are often prepared by the addition of minor amounts of low molecular weight tackifiers. Common tackifiers include polybutylenes, mono- and diglycerides of fatty acids, amorphous polypropylenes, terpene resins and rosin esters. Tackifiers are non-film-forming, migratory materials that can cause die lip build-up during film fabrication and other undesirable accumulations on equipment during wrapping operations that necessitates periodic stoppage of operations for cleaning and maintenance. Moreover, tackifiers often migrate to adjacent and opposite film layers and cause the aforementioned undesired adhesion and dirt retention problems commonly associated with two-sided cling films.

U.S. Pat. No. 5,093,188 teaches cling films comprising blends and/or multilayer constructions of chemically distinct polymers. An example of a cling film based on chemically distinct polymers is disclosed in U.S. Pat. No. 5,172,343 where an ethylene acrylate cling layer is used opposite a polypropylene or polyethylene non-cling layer. However, the use of functional polymers such as ethylene acrylate polymers and ethylene vinyl acetate polymers can present rheology matching problems in coextrusions with linear polyethylene as well as thermal instability and incompatibility problems during recycling of edge trim and film scrap generated during the film fabrication step. While rheological, instability and incompatibility problems can be mitigated to some extent by the use of extrusion-grafted linear polyethylene polymers as the functional polymer layer, as opposed to using the more common high-pressure autoclave produced polymers, these problems are not completely eliminated by employing the extrusion-grafted linear polyethylene polymers.

The addition of tackifiers or the use of functional polymer layers are allegedly not required for some prior art films. For example, EPO 0 287 272 discloses cling films can be prepared from heterogeneously branched linear low density polyethylene (LLDPE) with relatively high levels of n-hexane extractables. Preferred LLDPE polymers have a density in the range of 0.905 grams per cubic centimeter (g/cc) to 0.940 g/cc. However, these films tend to show inconsistent cling properties as well as the accumulation and migration shortcomings generally associated with cling films prepared by the addition of tackifiers.

Stretch wrap films having only one outer layer with substantial cling properties are known as one-sided cling films. Ordinarily, the obverse layer is the "non-cling" layer of the one-sided cling film and it forms the exterior of a package or wrapped article.

One-sided cling films can be prepared by corona discharge treatment of monolayer and multilayer films. However, as indicated in U.S. Pat. No. 4,425,268, functional polymers and copolymers are still required to obtain the desired cling properties. As such, and since functional polymers generally do not exhibit sufficient strength properties for stretch wrapping operations, multilayer constructions involving high strength linear polyethylene layers are more frequently used.

Typical multilayer constructions comprise an A/B or A/B/C film structure where the A layer is the cling or reverse layer and the B layer (or the C layer in an A/B/C construction wherein the B layer is a core or structural layer) is the non-cling or obverse layer. However, as discussed above, multilayer cling films usually comprise polymers with high levels of n-hexane extractables, low molecular weight tackifiers, or functional ethylene polymers or grafted polymers, or combinations thereof. There

are several disclosures that relate to such multilayer cling films, including US Pat. Nos. 3,501,363 3,508,944, 3,817,821, 3,986,611, 4,022,646, 4,082,877, 4,303,710, 4,348,455, 4,399,180, 4,364,981, 4,379,197 4,418,114, 4,425,268, 4,436,788, 4,504,434, 4,518,654, 4,542,188, 4,588,650, 4,612,221, 4,671,987, 4,833,017, 4,923,750, 5,049,423, 5,066,526, 5,093,188, 5,114,763, 5,141,809, 5,175,049, 5,208,096, and 5,212,001. While multilayer films are most often used for stretch cling wrapping operations, the multilayer construction in itself does not resolve the aforementioned deficiencies. These deficiencies are largely due to polymer selection and their respective chemistries and, generally, are not due to how the materials are brought together or fabricated into film.

Multilayer films can be successfully produced by number of well known methods including coextrusions and hot nip and adhesive film laminations as described in the various references incorporated herein. Load palletization can also be successfully accomplished manually or by a number of automated methods including the methods and apparatus described in U.S. Pat Nos. 5,054,263, 5,020,300, 4,779,396, and 4,754,594. However, overall deficiencies of inconsistent cling properties, die lip build-up, accumulations on equipment, and recycle incompatibility continue to persist in the art of stretch cling films.

The terms "homogeneous branching distribution" and "homogeneously branched" are defined herein to mean that (1) the α-olefin monomer is randomly distributed within a given molecule, (2) substantially all of the copolymer molecules have the same ethylene-to-α-olefin monomer ratio, (3) the polymer is characterized by a narrow short chain branching distribution wherein the composition distribution branch index is greater than 30 percent, preferably greater than 50 percent, (4) the

polymer essentially lacks a measurable high density (crystalline) polymer fraction as measured by known fractionation techniques such as, for example, a method that involves polymer fractional elutions as a function of temperature, and (5) the polymer is characterized as having substantially reduced levels of n-hexane extractables or substantial amorphism as determined by the FDA test method published as CFR 177.1520(c). By substantial amorphism, it is meant that greater than 75 weight percent of the whole polymer is soluble under prescribed test conditions.

The term "narrow short chain distribution" as applied herein pertains to the distribution of α-olefin monomer branches of the polymer as characterized by its SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index). The term is defined herein as greater than about 30 weight percent of the polymer molecules have an α-olefin monomer content within 50 percent of the median total molar α-olefin monomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, by Wild et al., Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or in US Patent 4,798,081.

The term "film-forming" is defined herein to mean the material or polymer has sufficient molecular weight and melt strength to allow a practitioner to conveniently fabricate it as a monolayer film or coextrusion layer on conventional extrusion equipment using conventional techniques without the addition of another material, another polymer or a processing aid.

The term "linear polyethylene" is defined herein as an ethylene polymer characterized as have no long chain branching as defined hereinabove. The term does not refer to high pressure, free-radical polymerized polyethylenes such as low density polyethylene (LDPE), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, or ethylene/vinyl alcohol (EVOH) copolymers which are known to those skilled in the art to have numerous long chain branches.

The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like, where, at least one other monomer is interpolymerized with ethylene to make the polymer.

The term "substantially linear" means that the polymer backbone is substituted with 0.01 long chain branch/1000 carbons to 3 long chain branches/1000 carbons, more preferably from 0.01 long chain branch/1000 carbons to 1 long chain branch/1000 carbons, and especially from 0.05 long chain branch/1000 carbons to 1 long chain branch/1000 carbons.

The term "long chain branched" is defined herein as a chain length of at least about 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy, yet the long chain branch can be about the same length as the length of the polymer back-bone. Long chain branching is determined by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method described by Randall (Rev. Macromol. Chem. Phys., C29, V. 2&3, p. 285-297).

The term "ultra low density polyethylene" (ULDPE) is also known in the linear polyethylene art as "very low density polyethylene" (VLDPE) and "linear very low density polyethylene" (LVLDPE) and herein designates a density less than about 0.915 g/cc. "Medium density

polyethylene" (MDPE) is also known in the art as "linear medium density polyethylene" and herein designates a density in the range of 0.930 to 0.945 g/cc. "Linear low density polyethylene" (LLDPE) herein designates a density in the range of 0.916 to 0.929 g/cc. "High density polyethylene" (HDPE) herein designates a density greater than about 0.945 g/cc.

The term "non-cling" is defined herein as the amount of cling of a given layer that is insufficient to obtain a good self-seal when used in stretch cling operations although the layer may actually exhibit a small amount of measurable cling.

The density of the various polymers used to make the multilayer one-sided cling film of the present invention is measured in accordance with ASTM D-792 and is reported as g/cc.

The film of the present invention is tested for reverse layer-to-obverse layer cling and obverse layer-to-obverse layer cling according to ASTM D 4649 § A.3 & A1.2.3, Test Methods for Peel Cling of Thin Films and is reported as the force in grams required to separate two strips of film. For stretched-film cling determinations, a 1" x 7" (25 mm x 178 mm) strip of the film to be tested is stretched 200 percent and attached to a 20 degree inclined plane with the obverse layer (non-cling) facing upward. A second, unstretched 1" x 7" (25 mm x 178 mm) strip of film is placed on top of the first strip with the reverse layer or another obverse layer facing downward. Sufficient pressure is applied with a brush to cause the two strips to adhere together. The end of the second strip at the base of the incline plane is attached, by a clip and a string, to an apparatus which can exert a strain at a constant rate, such as an Instron Tensile Tester. The two strips are separated at a crosshead speed of 5 inches/minute (13 centimeters/minute) until the attached string is parallel with the base of

the inclined plane. In general, stretched cling values are appreciable less than unstretched values.

Melt index measurement is performed according to ASTM D-1238, Condition 190°C/2.16 kilogram (kg), formerly known as "Condition E" and also known as I_2. Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. Melt index is reported as g/10 minutes.

Melt index determinations can also be performed with higher weights, such as in accordance with ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition N" and also known as I_{10}). The term "melt flow ratio" as defined herein is the ratio of a higher weight melt index determination to a lower weight determination, and for measured I_{10} and the I_2 melt index values, the melt flow ratio is conveniently designated as I_{10}/I_2.

The present invention is a novel multilayer film comprising at least two layers, having substantial cling properties on one side and adapted for use as a stretch wrapping material. The new multilayer film comprises: a reverse layer comprising at least one film-forming homogeneously branched ethylene polymer composition having a density of about 0.90 g/cc or less than about 0.90 g/cc, an obverse layer comprising at least one film-forming olefin polymer composition having a density above about 0.90 g/cc, and, optionally, at least one core or structural layer comprising at least one high strength ethylene polymer composition.

The obverse layer exhibits significantly less cling than the reverse layer. The core or structural layer can be varied to meet application-specific film strength requirements.

In accordance with the present invention, film prepared with one-sided cling properties are especially useful in stretch wrapping, stretch-bundling and tension-winding operations for wrapping or holding small and large goods. The one-sided cling film of the present invention is provided without the need for tackifying additives or functional polymers.

The benefits of this invention includes: substantially reduced or eliminated: die-lip build, accumulation and migration of low molecular weight materials. This means that cleaning and maintenance time will be reduced during film fabrication and wrapping operations. Problems pertaining to adhesion to adjacent goods and packages as well as surface retention of dirt, dust and debris will also be reduced.

Another aspect of this invention is to provide a one-sided cling film comprising polymers with similar rheologies and monomer chemistries, and thereby facilitate improved melt viscosity matching during coextrusions and good polymer compatibility for recycling purposes.

Another aspect of this invention is to provide a one-sided cling film where high cling is not diminished when the film is under stretched conditions such that the inventive film shows equivalent stretched and unstretched cling properties.

FIG. 1 is a graph that corresponds to the data in Table 4 and relates the density of homogeneously branched ethylene polymers to the reverse-to-obverse cling properties of unstretched and stretched A/B/C multilayer films.

It has been discovered that the amount of cling relates to the density of the polymer or blend combination that forms the reverse and obverse layers of the film; as density of the polymer in the reverse layer is decreased, cling properties improve. A reverse layer of this invention will

show substantial cling to an obverse layer when the density of the reverse layer is 0.90 g/cc or less, preferably in the range of 0.85 g/cc to 0.89 g/cc, and more preferably, in the range of 0.86 g/cc to 0.88 g/cc. The density of an obverse layer of this invention is greater than 0.90 g/cc, preferably in the range of 0.91 g/cc to 0.96 g/cc, and more preferably, in the range of 0.93 g/cc to 0.95. Obverse layers in the more preferred density range of 0.93 g/cc to 0.95 g/cc provide one-sided cling films with equivalent stretch and unstretched cling properties.

The density of a core layer or structural layers included in the multilayer film of this invention can be varied to meet total film strength requirements depending on the end-use application.

The film-forming homogeneously branched ethylene polymer composition having a density of 0.90 g/cc or less than 0.90 g/cc that comprise the reverse layer of the present invention includes homogeneously branched very low density polyethylene (VLDPE), substantially linear ethylene polymers and blend combinations thereof. Preferably, the reverse layer comprises a substantially linear ethylene polymer and, more preferably, the substantially linear ethylene polymer is prepared by a solution process wherein ethylene is polymerized with 1-octene. Substantially linear ethylene polymers are preferred due to their favorable rheological properties.

The film-forming homogeneously branched ethylene polymers used to form the multilayer film of the present invention will show reduced n-hexane extractables that generally increase at a low level as polymer density is decreased. However, surprisingly at polymer densities less than 0.90 g/cc, these polymers become substantially amorphous and yet can be readily formed into wrapping films.

The film-forming olefin polymer composition having a density greater than 0.90 g/cc that comprise the obverse layer of the present invention includes propylene and ethylene polymers such as polypropylene, ethylene propylene copolymers, low density polyethylene (LDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), substantially linear ethylene polymers, heterogeneously and homogeneously branched linear low density polyethylene (LLDPE), heterogeneously and homogeneously branched very low density polyethylene (VLDPE), and blend combinations thereof. Preferably, the obverse layer comprises polypropylene, such as, for example, polypropylene in blend combination with MDPE or HDPE MDPE alone. can also be used and is preferred due to its ability to provide equivalent stretched and unstretched cling properties.

The ethylene polymer that comprise a core or structural layer of the present invention includes low density polyethylene (LDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), substantially linear ethylene polymers, heterogeneously and homogeneously branched linear low density polyethylene (LLDPE), heterogeneously and homogeneously branched very low density polyethylene (VLDPE). Preferably, the core or structural layer comprises fractional melt index low density polyethylene or LLDPE, more preferably, linear low density polyethylene (LLDPE) and, most preferably, the LLDPE is prepared by a solution process wherein ethylene is polymerized with 1-octene. LLDPE is preferred due to its known superior film strength properties.

Heterogeneously branched VLDPE and LLDPE are well known among practitioners of the linear polyethylene art. They are prepared using Ziegler-Natta solution, slurry or gas phase polymerization processes and coordination metal catalysts as described, for example, by Anderson et al. in U.S. Pat. No. 4,076,698. These Ziegler-type linear polyethylenes are not homogeneously branched and they do not have any long-chain branching. Also, these polymers do not show any substantial amorphism at lower densities since they inherently posses a substantial high density (crystalline) polymer fraction. At a density less than 0.90 g/cc, these materials are very difficult to prepare using conventional Ziegler-Natta catalysis and are also very difficult to pelletize. The pellets are tacky and tend to clump together.

Homogeneously branched VLDPE and LLDPE are also well known among practitioners of the linear polyethylene art. See, for example, Elston disclosure in U.S. Pat. No. 3,645,992. They can be prepared in solution, slurry or gas phase processes using zirconium and vanadium catalyst systems. Ewen et al. in U.S. Pat. No. 4,937,299 described a method of preparation using metallocene catalysts. This second class of linear polyethylenes are homogeneously branched polymers, but like the Ziegler-type heterogeneous linear polyethylene, they do not have any long-chain branching. Commercial examples of these polymers are sold by Mitsui Chemical under the designation "TAFMER" and by Exxon Chemical under the designation "EXACT".

The substantially linear ethylene polymers used in the present invention are a unique class of compounds that are further defined in U.S. Pat. No. 5,272,236 and in U.S. Pat. No. 5,278,272. The teachings disclosed in these copending applications include the utilization of constrained

geometry catalysts and suitable methods of production.

Substantially linear ethylene polymers are homogeneously branched but, unlike other homogeneously branch ethylene polymers, substantially linear ethylene polymers are characterized as having long chain branching and as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

c) a critical shear rate at onset of surface melt fracture at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of either a homogeneously or heterogeneously branched linear ethylene polymer having about the same I_2 and M_w/M_n.

A unique characteristic of the substantially linear ethylene polymers used to prepare the multilayer stretch wrap materials of this invention is a highly unexpected flow property where the I_{10}/I_2 value of the polymer is essentially independent of the polydispersity index (that is M_w/M_n) of the polymer. This is contrasted with linear homogeneously branched and linear heterogeneously branched polyethylenes which have rheological properties such that as the I_{10}/I_2 value increases, the respective polydispersity index also increases. In addition, substantially linear ethylene polymers also exhibit enhanced processability as manifested by a higher extrusion output, lower pressure drop through screen packs and gel filters, lower extruder amperage and lower die pressure as well as excellent melt strength and non-tackiness at lower polymer densities that permit efficient pelletization.

The film-forming homogeneously branched ethylene polymer compositions used for the reverse layer, and the film-forming olefin

polymer composition used for the obverse layer, and the high strength ethylene polymer composition used for the core or structural layer of this invention are ethylene polymers which are prepared by homopolymerizing ethylene or interpolymerizing ethylene with a minor amount of a variety of monomers. Suitable such monomers include ethylenically unsaturated monomers, conjugated or non-conjugated dienes, and polyenes. Examples of such comonomers include C_3-C_{20} α-olefins as propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene. Preferred comonomers include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene, and 1-octene is especially preferred. Other suitable monomers include styrene, halo- or alkyl-substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, 1,7-octadiene, and cycloalkenes, for example, cyclopentene, cyclohexene and cyclooctene.

Additives such as cling additives and tackifiers (for example, PIB), slip and antiblock agents, antioxidants (for example, hindered phenolics such as Irganox® 1010 or Irganox® 1076 supplied by Ciba Geigy), phosphites (for example, Irgafos® 168 also supplied by Ciba Geigy), Standostab PEPQ™ (supplied by Sandoz), pigments, colorants, fillers, and processing aids, although not required to achieve the desired results of this invention, can also be included in the stretch wrapping material disclosed herein. However, the additives should incorporated in such manners or to the extent that they do not interfere with the substantial cling and non-cling properties discovered by Applicants.

The multilayer film of the present invention may be constructed from two or more film layers including A/B and A/B/C film structures by any film lamination and/or coextrusion technique and any blown or cast

film extrusion equipment known in the art. However, the preferred construction is an A/B/C structure prepared by coextrusion techniques, and, more preferably, by cast coextrusion techniques.

Suitable blown film processes are described, for example, in The Encyclopedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416-417 and Vol. 18, pp. 191-192. A suitable cast extrusion method is described, for example, in Modern Plastics Mid-October 1989 Encyclopedia Issue, Volume 66, Number 11, pages 256 to 257. Suitable coextrusion techniques and requirements are described by Tom I. Butler in Film Extrusion Manual: Process, Materials, Properties, "Coextrusion", Ch. 4, pp. 31-80, TAPPI Press, (Atlanta, Ga. 1992).

The melt index of each polymer layer of the multilayer film of this invention is in the range of 0.4 to 20 g/10 minutes, preferably, in the range of 0.5 to 12 g/10 minutes and, more preferably, in the range 0.8 to 6 g/10 minutes.

The total film thickness of the multilayer film of the present invention is in the range of 0.4 to 20 mils (10 microns to 508 microns), preferably, in the range of 0.6 to 10 mils (15 microns to 254 microns) and, more preferably, in the range of 0.8 to 5 mils (20 microns to 127 microns).

The layer ratio for the A/B multilayer film of this invention is greater than 2:98 A layer to B layer, preferably range from 5:95 to 35:65 and, more preferably, range from 10:90 to 25:75. The ratio layer of multilayer films having more than two layers is such that the reverse and obverse layers of the film is maintained at the same thickness and the ratio of core

or structural layer is ranges from 60 to 98 weight percent, preferably range from 65 to 95 weight percent, and more preferably range from 70 to 90 weight percent.

Ziegler-type heterogeneously branched linear ethylene α-olefin polymers inherently possess relatively high levels of n-hexane extractables that permit substantial cling properties. In the density range of 0.905 g/cc to 0.930 g/cc, these polymers at 2 mil (51 microns) film thickness typically possess 1.3 to 3.0 weight percent n-hexane extractable when measured according to the FDA test method published as CFR 177.1520(c). At densities in the range of 0.86 to 0.90 g/cc, these polymers are soluble in under test conditions up to a maximum of about 65 weight percent. Conversely, Table 1 shows that homogeneously branched ethylene polymers possess relatively low levels of n-hexane extractables at densities greater than about 0.90 g/cc, and are substantially amorphous at a density of about 0.90 g/cc, and completely amorphous at a density of 0.88 g/cc or less.

Homogeneously Branched Substantial
Linear Ethylene/1-Octene Copolymers

Density, g/cc	Percent Extractables (by weight)
0.95	0.1
0.94	0.2
0.92	0.4
0.91	0.8
0.90	Approx. 90 percent Soluble Under Test Conditions
0.88	100 percent Soluble Under Test Conditions

Examples

The following examples illustrate some of the particular embodiments of the present invention, but the following should not be construed to mean the invention is limited to the particular embodiments shown.

Examples 1-7

Table 2 summarizes the polymers used in an A/B/C cast coextrusion film evaluation.

Table 2

Resin	I_2 g/10 min.	Density g/cc	Polymer/Composition Description
SLEP 1	3.0	0.875	A homogeneously branched substantially linear ethylene/ 1-octene copolymer prepared by a solution polymerization process
SLEP 2	5.0	0.870	A homogeneously branched substantially linear ethylene/ 1-octene copolymer prepared by a solution polymerization process
SLEP 3	3.0	0.910	A homogeneously branched substantially linear ethylene/ 1-octene copolymer prepared by a solution polymerization process
SLEP 4†	3.0	0.900	A blend of 71.4 wt. percent SLEP 3 + 28.6 wt. percent SLEP 1
SLEP 5†	3.0	0.887	A blend of 35 wt. percent SLEP 3 + 65 wt. percent SLEP 1
SLEP 6†	3.0	0.882	A blend of 20 wt. percent SLEP 3 + 80 wt. percent SLEP 1
SLEP 7	3.0	0.900	A homogeneously branched substantially linear ethylene/ 1-octene copolymer prepared by a solution polymerization process
VLDPE	3.2	0.900	A homogeneously branched very low density ethylene/ 1-butene interpolymer prepared by a gas-phase polymerization process and sold by Exxon Chemical Company under designation the "Exact 3027".
EMA	4.6	0.945	An ethylene methacrylate copolymer containing about 25 weight percent methacrylate and sold by Exxon Chemical Company under the designation "XC-102".
HDPE	7.0	0.954	A high density polyethylene prepared by a solution polymerization process and sold by The Dow Chemical Company under the designation "HDPE 08354N"
LLDPE 1	2.3	0.917	A heterogeneously branched linear low density ethylene/ 1-octene copolymer prepared by a solution polymerization process and sold by The Dow Chemical Company under the designation "DOWLEX 3347A"
LLDPE 2	1.0	0.920	A heterogeneously branched linear low density ethylene/ 1-octene copolymer prepared by a solution polymerization process and sold by The Dow Chemical under the designation "DOWLEX 2245A"
MDPE	4.0	0.941	A medium density polyethylene prepared by a solution polymerization process and sold by The Dow Chemical Company under the designation "DOWLEX 2027A"
PP†	4.7	0.921	A blend of an isotactic polypropylene sold by Exxon Chemical Company under the designation "PP 4062" blended + a solution process HDPE sold by The Dow Chemical Company under the designation "HDPE 08354N"
LDPE†	2.6	0.920	A blend of a low density polyethylene prepared by a tubular process and sold by The Dow Chemical Company under the designation "LDPE 748I" + a solution LLDPE sold by The Dow Chemical Company under the designation "DOWLEX 2245A"

†Polymer blend composition prepared by tumble dry-blending, however any known polymer blending technique is suitable for use with the present invention including, for example, extrusion melt blending.

Example 1

One multilayer stretch cling film that is exemplary of a film commercially used in the industry was prepared using EMA as the reverse layer, LLDPE 1 as the core or structural layer and PP as the obverse layer. The cast coextrusion film equipment utilized to prepare this comparative sample consisted of a three extruder configuration: a 3-1/2 inch (8.9 cm) diameter Egan primary extruder ("B" core or structural layer) with a 32:1 L/D; a 2-1/2 inch (6.4 cm) diameter Egan satellite extruder ("A" reverse layer) with a 24:1 L/D; and a 2 inch (5.1 cm) diameter Davis Standard satellite extruder ("C" obverse layer) with a 24/1 L/D. The molten polymer exited the extruders through an A/B/C feedblock into a 30 inch (76.2 cm) Johnson coat-hanger, flex-lip slot die. The pumping rates of the extruders were adjusted to maintain a 15 percent/70 percent/15 percent film layer thickness ratio as molten polymer was fed through a 0.020 inch (0.05 cm) die gap. The coextruded film contacted two chill rolls cooled to 70°F (21°C) at an air/draw gap of 5 inches (12.7 cm).

The cast coextruded film sample was conveniently produced at a nominal total film thickness of 0.8 mil (20 microns), a melt temperature of approximately 400°F (204°C) for the A layer and 525°F (274°C) for B and C layers, and a line speed of 800 feet per minute (244 meters per minute). The resultant film had an unstretched reverse layer-to-obverse layer cling value of 123 grams and a stretched cling value of 47 grams according to ASTM D-4649 § A.3.

Table 3 summarizes A/B/C coextruded film constructions of Examples 2-5 of the present invention. The multilayer films were conveniently prepared using the same equipment and settings indicated in Example 1. Extrusion processability was excellent and no die-lip build-

up was observable during a 2-hour fabrication trial of these film structures. ASTM D-4649 § A.3 unstretched and 200 percent stretched cling results for these examples are presented in Table 4.

Table 3

Example	Layer A	Layer B	Layer C
2	SLEP 1	LLDPE 1	PP
3	SLEP 2	LLDPE 1	PP
4	SLEP 2	LLDPE 1	MDPE
5	SLEP 5	LLDPE 1	PP

Table 4

Example	A Layer Density	Unstretched Cling (g)	200 percent Stretched Cling (g)
2	0.875	252	122
3	0.870	360	220
4	0.870	339	356
5	0.887	52	0

The data in Table 4 demonstrate that films prepared in accordance with the present invention exhibited substantial cling in both the unstretched and the 200 percent stretched condition. Surprisingly, the film structures that comprise a substantially linear polymer as the cling layer and MDPE as the non-cling layer exhibited (Example 4) equivalent or higher cling values in the 200 percent stretched condition as compared to the unstretched condition. Furthermore, at a density less than 0.88 g/cc (Examples 2-5), the cling properties of the film of this invention were superior to commercially representative film, Example 1. The inventive films also exhibited good physical properties.

<u>Examples 6-8</u>

An additional cast film evaluation was conducted using the same equipment and extrusion parameters as Example 1 except the "A" reverse layer extruder was operated to provide a melt temperature of 500°F (260°C)

instead of 400°F (204°C). Table 5 summarizes the samples that were used for this evaluation.

Table 5

Example	Layer A	Layer B	Layer C
6	SLEP 1	LLDPE 1	PP
7	SLEP 6	LLDPE 1	PP
8	SLEP 7	LLDPE 1	PP

Table 6 summarizes the cling layer density (Layer A), and unstretched and 200 percent stretched cling values for Examples 6-8.

Table 6

		Reverse-to-Obverse Cling, g	
Example	A Layer Density, g/cc	Unstretched	Stretched
6	0.875	280	177
7	0.882	141	77
8	0.888	72	36

As Table 6 illustrates, at higher melt temperatures, the film-forming homogeneously branched substantially linear ethylene polymers (Examples 6-8) exhibited substantial cling properties at a density as high as about 0.89 g/cc. However, the higher fabrication temperature did not produce any observable die lip build-up or accumulation on equipment parts which is normally associated with polymers in the prior art which contain tackifiers and high level of n-hexane extractables.

Examples 9-10

In another evaluation, A/B/C film structure were prepared by a blown coextrusion technique. The blown film coextrusion equipment

utilized to fabricate Examples 9 and 10 consisted of a three extruder configuration: a 2-1/2 inch (6.4 cm) 60 horsepower Egan outer layer extruder (A layer), a 2-1/2 inch (6.4 cm) 75 horsepower Egan core layer extruder (B layer) and a 2 inch (5.1 cm) Johnson 20 horsepower inner layer extruder (layer C). Molten polymer exited the extruders into a Johnson three-layer 8 inch (20.3 cm) coextrusion spiral mandrel die fitted with a die pin and a 0.07 inch (70 mil) die gap. The pumping rates of the extruders were adjusted to maintain a 15 percent/70 percent/15 percent film layer thickness ratio.

Both coextruded blown film samples were conveniently produced at a nominal total film thickness of 0.8 mil (20 microns), a melt temperature of approximately 360°F (182°C) for the A layer extruder, 430°F (221°C) for the B layer extruder, and 400°F (204°C) for the C layer extruder. Evaluations were conducted at a blow-up ratio (BUR) of 2:1 and a line speed of 170 feet per minute (52 meters per minute). Table 7 summarizes the coextruded blown film structures.

Table 7

Example	Layer A	Layer B	Layer C
9	SLEP 1	LLDPE 2	LDPE
10*	EMA	LLDPE 2	LDPE

*Not an example of the present invention; provided for comparative purposes only.

Table 8, which summarizes the ASTM D-4649 unstretched and 200 percent stretched cling values for examples 9-10, indicates similar to the multilayer cast film of the present invention, our inventive blown film (Example 9) exhibited significantly better cling properties than a commercially representative film structure (Example 10).

Table 8

Example	Unstretched Cling, g	200 percent Stretched Cling, g
9	142	110
10	80	52

Examples 11-14

In another cast coextrusion evaluation employing the same coextrusion equipment and parameters as described for Examples 1, A/B film structures were prepared. In this evaluation, the both B layer and C layer extruders were operated to provide the obverse and the A extruder was operated to provide the reverse layer. The layer ratio was maintained at 15:85 A/B layers. The nominal total film thickness was 0.8 mils. Table 9 summarizes the respective layer configurations as well as the cling properties for these structures. Table 9 indicates, multilayer film prepared according to the present invention with either a homogeneously branched substantially linear ethylene polymer (Examples 13 and 14) or a homogeneously branched linear ethylene polymer (Examples 15 and 16) exhibited good unstretched cling properties at a reverse layer polymer density of about 0.90 g/cc. In addition, Table 9 indicates that its cling performance was also superior to a comparative film having a reverse layer polymer density of about 0.91 g/cc (Example 12).

Table 9

Example	Reverse	Obverse	Reverse to Obverse Cling Unstretched, g
12*	SLEP 3	LLDPE 2	0
13	SLEP 7	LLDPE 2	57
14	SLEP 7	HDPE	45
15	VLDPE	LLDPE 2	37
16	VLDPE	HDPE	28

*Not an example of the present invention in that the density of SLEP 3 0.91 g/cc.

Table 10 compares the film physical properties of the comparative Example 1 film and the Inventive Example 2 film. The comparison indicates that multilayer film made in accordance with the invention disclosed herein exhibited film optical and strength properties equivalent to a commercially representative film, Example 1.

Table 10

Property		Example 1*	Example 2	Test Method
45° Gloss		62	66	ASTM D-2457
Percent Haze		5.76	4.32	ASTM D-1003
Dart Impact, g		115	149	ASTM D-1709 (METHOD A)
Puncture, ft-lb/in^3 (kg-cm/cm^3)		183 (131)	191 (161)	Described Below
Tensile Strength, psi (MPa)				
	MD	7,108 (49.0)	7,666 (52.8)	ASTM D-882
	CD	4,574 (31.5)	3,158 (21.7)	
	MD	1,397 (9.6)	1,279 (8.8)	ASTM D-882
	CD	1,211 (8.3)	1,074 (7.4)	
Percent Elongation				
	MD	478	524	ASTM D-882
	CD	739	634	

*Not an example of the present invention; provided for comparative purposes only.

Puncture was determined using a Instron Model 4201 Tensiometer fitted with a film specimen holder at its lower jaw and a semi-spherical aluminum tip probe at its upper jaw. The tensiometer was operated at cross-head speed of 25 mm/minute and utilizes a 45 kg load cell.

In an observed cling evaluation according to ASTM D-4649 § A1.2.3, the multilayer films of Inventive Examples 2-5 were tested for cling performance. The equipment used for this evaluation was a Lantech Model SHS Power Pre-Stretch Pallet Wrapper set for 200 percent film pre-stretching and 200 percent on-pallet film stretching. The palletization load consisted of a 500-pound (227-kilogram) 5 foot x 4 foot x 4 foot (1.5 meter x 1.2 meter x 1.2 meter) angle-iron frame. Each film was separately wrapped five times about the frame and thereafter slit cut and checked for respective cling properties. All of the Inventive Examples (Examples 2-5) exhibited "excellent cling" in this evaluation.

Claims :

1. A multilayer cling-wrap film comprising at least a reverse layer and an obverse layer,

the reverse layer comprising at least one film-forming homogeneously branched ethylene polymer composition having a density of about 0.90 g/cc or less,

and the obverse layer comprising at least one film-forming olefin polymer composition having a density greater than about 0.90 g/cc.

2. The multilayer film of Claim 1, wherein the film is an A/B two layer structure.

3. The multilayer film of Claim 1, wherein the film additionally comprises at least one core or structural layer.

4. The multilayer film of Claim 3, wherein the core or structural layer comprises at least one ethylene polymer composition.

5. The multilayer film of Claim 3, wherein the film is an A/B/C three layer structure.

6. The multilayer film of Claim 1, wherein the at least one homogeneously branched ethylene polymer composition of the reverse layer is a substantially linear ethylene polymer characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$,

c) a critical shear rate at onset of surface melt fracture of at

least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n, and

7. The multilayer film of Claim 1, wherein the at least one homogeneously branched ethylene polymer composition of the reverse layer is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

8. The multilayer film of Claim 1, wherein the at least one homogeneously branched ethylene polymer composition of the reverse layer is a linear very low density polyethylene.

9. The multilayer film of Claim 1, wherein the density of the reverse layer is from 0.85 g/cc to 0.89 g/cc.

10. The multilayer film of Claim 1, wherein the at least one olefin polymer of the obverse layer is a propylene or ethylene polymer.

11. The multilayer film of Claim 1, wherein the at least one olefin polymer of the obverse layer is a linear ethylene α-olefin interpolymer.

12. The multilayer film of Claim 1, wherein the obverse layer comprises polypropylene and high density polyethylene.

13. The multilayer film of Claim 1, wherein the obverse layer comprises high pressure low density polyethylene and linear low density polyethylene.

14. The multilayer film of Claim 1, wherein the density of the obverse layer is from 0.91 g/cc to 0.96 g/cc.

15. The multilayer film of Claim 4, wherein the at least one ethylene polymer composition is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

16. The multilayer film of Claim 4, wherein the at least one ethylene polymer composition is linear ethylene/α-olefin interpolymer.

17. In a method for making a multilayer one-sided cling-wrap film having at least two layers, comprising the steps of:

(i) feeding an ethylene polymer composition into a reverse layer coextrusion extruder,

(ii) feeding an ethylene polymer composition into a obverse layer coextrusion extruder,

(iii) additionally feeding an ethylene polymer composition into a core or structural layer coextrusion extruder,

(iv) melting and mixing the polymer compositions at a melt temperatures greater than about 177°C to form at least two molten polymer streams,

(v) adjusting the extrusion output such that at least 5 percent by weight of the total extrusion output constitutes the reverse layer molten polymer stream,

(vi) extruding the molten polymer streams through a

coextrusion feedblock into a slot die to form a web or into an annular die to form a tube having a reverse layer and an obverse layer,

(vii) blowing up and cooling said tube or drawing down and cooling said web to make said multilayer film (viii) collecting said multilayer film for subsequent use,

the improvement comprising feeding to the reverse layer coextrusion extruder at least one film-forming homogeneously branched ethylene polymer composition having a density of about 0.90 g/cc or less and feeding to the obverse layer coextrusion extruder a film-forming olefin polymer composition having a density greater than 0.90 g/cc.

18. In a stretch-wrapping operation comprising the steps of:

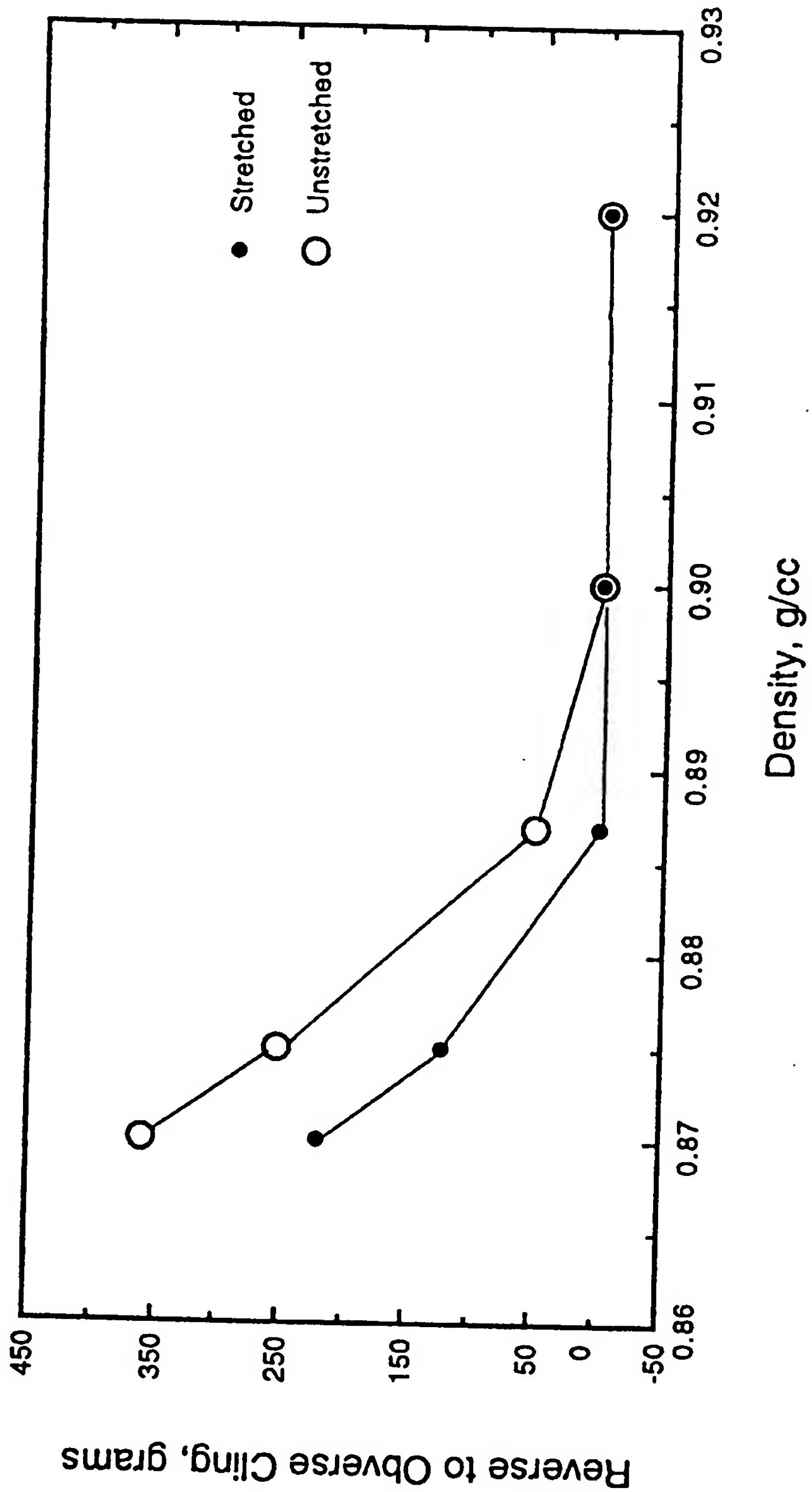
(i) attaching a film onto an automated or manual wrapping device,

(ii) wrapping the film about articles or group of articles situated on a pallet, and

(iii) sealing the film to itself,

the improvement comprising using as said film a multilayer film comprising at least two layers wherein said layers comprise a reverse layer and an obverse layer, said reverse layer comprising at least one film-forming homogeneously branched ethylene polymer composition having a density of about 0.90 g/cc or less than about 0.90 g/cc, and said obverse layer comprising at least one film-forming olefin polymer composition having a density greater than about 0.90 g/cc.

FIG. I


Stretched
Unstretched
Density, g/cc
Reverse to Obverse Cling, grams
0.86
0.87
0.88
0.89
0.90
0.91
0.92
0.93
450
350
250
150
50
0
-50

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/14273

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/32 B65D65/40 //C08J5/18,C08L23/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B B65D C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,94 09060 (THE DOW CHEMICAL COMPANY) 28 April 1994 see page 37, line 14 - page 38, line 17; claims 1,2,16,18-21,42; examples 11,13 see page 2, line 27-35 - page 17, line 25-27	1-11, 13-18
Y	US,A,5 206 075 (HODGSON, JR.) 27 April 1993 see column 4, line 30-66 - column 3, line 1-49; claims 1,8-12,14,15	2-18
Y	US,A,5 093 188 (DOHRER) 3 March 1992 see the whole document	1-18
P,A	EP,A,0 600 425 (W.R. GRACE & CO.) 8 June 1994 see the whole document	1,6-9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 April 1995	26.04.95 26.04.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Derz, T

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Inte   onal Application No
PCT/US 94/14273

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	WO,A,93 03093 (EXXON CHEMICAL PATENTS INC.) 18 February 1993 see the whole document -----	1-18

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 94/14273

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